SAND2007-8024C

Basic Materials Studies of Lanthanide Halide Scintillators

F. P. Doty[1], Douglas McGregor[2], Mark Harrison[1,2], Kip Findley[3], Raulf Polichar[4] and Pin Yang[5]; [1]Engineered Materials Dept., Sandia National Laboratories, Livermore, California; [2]Dept. of Mechanical & Nuclear Engineering, Kansas State University, Manhattan, Kansas; [3]School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington; [4]SAIC, San Diego, California; [5]Ceramic & Glass Dept, Sandia National Laboratories, Albuquerque, New Mexico.

ABSTRACT

Cerium and lanthanum tribromides and trichlorides form isomorphous alloys with the hexagonal UCl3 type structure, and have been shown to exhibit high luminosity and proportional response, making them attractive alternatives for room temperature gamma ray spectroscopy. However the fundamental physical and chemical properties of this system introduce challenges for material processing, scale-up, and detector fabrication. In particular, low fracture stress and perfect cleavage along prismatic planes cause profuse cracking during and after crystal growth, impeding efforts to scale this system for production of low cost, large diameter spectrometers. We have reported progress on basic materials science of the lanthanide halides. Studies to date have included thermomechanical and thermogravimetric analyses, hygroscopicity, yield strength, and fracture toughness. The observed mechanical properties pose challenging problems for material production and post processing; therefore, understanding mechanical behavior is key to fabricating large single crystals, and engineering of robust detectors and systems. Analysis of the symmetry and crystal structure of this system, including identification of densely-packed and electrically neutral planes with slip and cleavage, and comparison of relative formation and propagation energies for proposed slip systems, suggest possible mechanisms for deformation and crack initiation under stress. The low c/a ratio and low symmetry relative to traditional scintillators indicate limited and highly anisotropic plasticity cause redistribution of residual process stress to cleavage planes, initiating fracture. Ongoing work to develop fracture resistant lanthanide halides is presented.

INTRODUCTION

Lanthanum halide scintillators have enabled scintillating gamma ray spectrometers competitive with room temperature semiconductors[1,2], providing similar energy resolution with larger active volumes than available CdZnTe detectors, making such applications as hand held radioisotope spectrometers practical [3]. However, increasing the active volume to larger sizes needed for applications in nuclear nonproliferation and homeland security has proven difficult due to profuse cracking during crystal growth and subsequent processing. Therefore basic studies of the materials science of the lanthanide halide system are needed to determine the causes of cracking, and develop strategies to scale the crystal growth.

RESULTS AND DISCUSSION

Cleavage

Results of materials property measurements made by Sandia National Laboratories and collaborators were recently reviewed[4],[5] and a strategy to strengthen these materials was proposed[6]. The key results were determination of the high degree of anisotropy of thermal expansion, plasticity, and fracture inherent to the crystal structure. In particular, the materials fail mechanically by brittle fracture, usually along very well defined cleavage planes

This anisotropy can be visualized in reference to the figure below, which represents adjacent lanthanide ion positions (green) in relation to some of the halogen ion positions (red). The rectangular faces of the prisms are parallel to the c-axis, and those faces adjoining the prisms represent the 11.0 planes of the hexagonal structure. These planes have been identified with the cleavage experimentally using electron diffraction. The weak bonding across these planes is partly due to the greater bond lengths between the lanthanide and coplanar halide ions, relative to the six above- and below-plane ions. Therefore the marked polygons slip vertically intact, with each lanthanide carrying its six nearest neighbors.

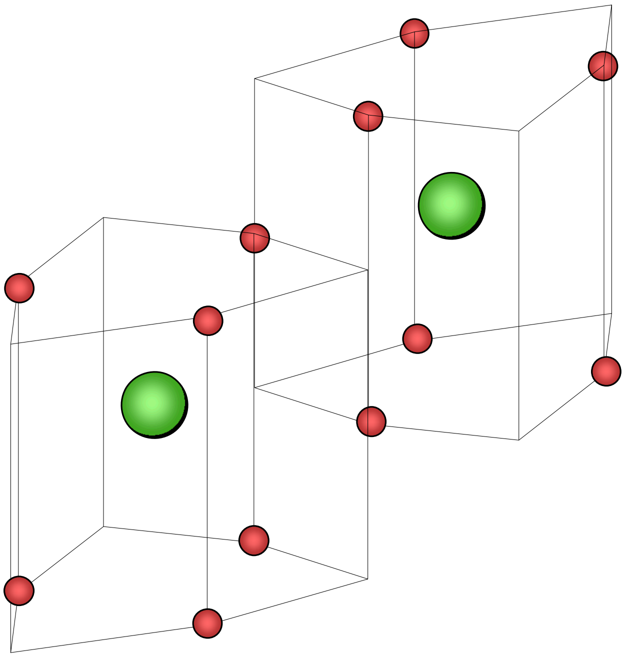

Figure 1. Polygons representing a portion of the LnX3 try structure (c-axis vertical). Both easy slip and cleavage are expected along the shared faces, which represent (11.0) planes in the hexagonal structure

This proposed mechanism is supported by consideration of the elastic strain energy associated with possible Burger's vectors for dislocations. The low c/a ratio indicates roughly 1/3 the energy for c-axis slip, relative to the basal plane. The high packing density and observed low bonding strength of the prismatic planes indicates that {11.0}<00.1> is the primary slip system. Since this Burger's vector is unique in the structure, plastic strain is predicted to be highly anisotropic. Therefore highly localized slip on the prismatic planes would be expected to cause dislocation pileups, building to critical flaws on these planes under relatively low stress. This problem would be exacerbated by the anisotropic expansion, causing shears to develop on these planes for temperature gradients not parallel to the c-axis.

The net effect of this anisotropy is to initiate cleavage fracture in single crystals with extremely low fracture work, as determined quantitatively by fracture toughness estimates. This parameter has been evaluated from microhardness indentations, and plotted against the estimated yield strength in Figure 2 below.

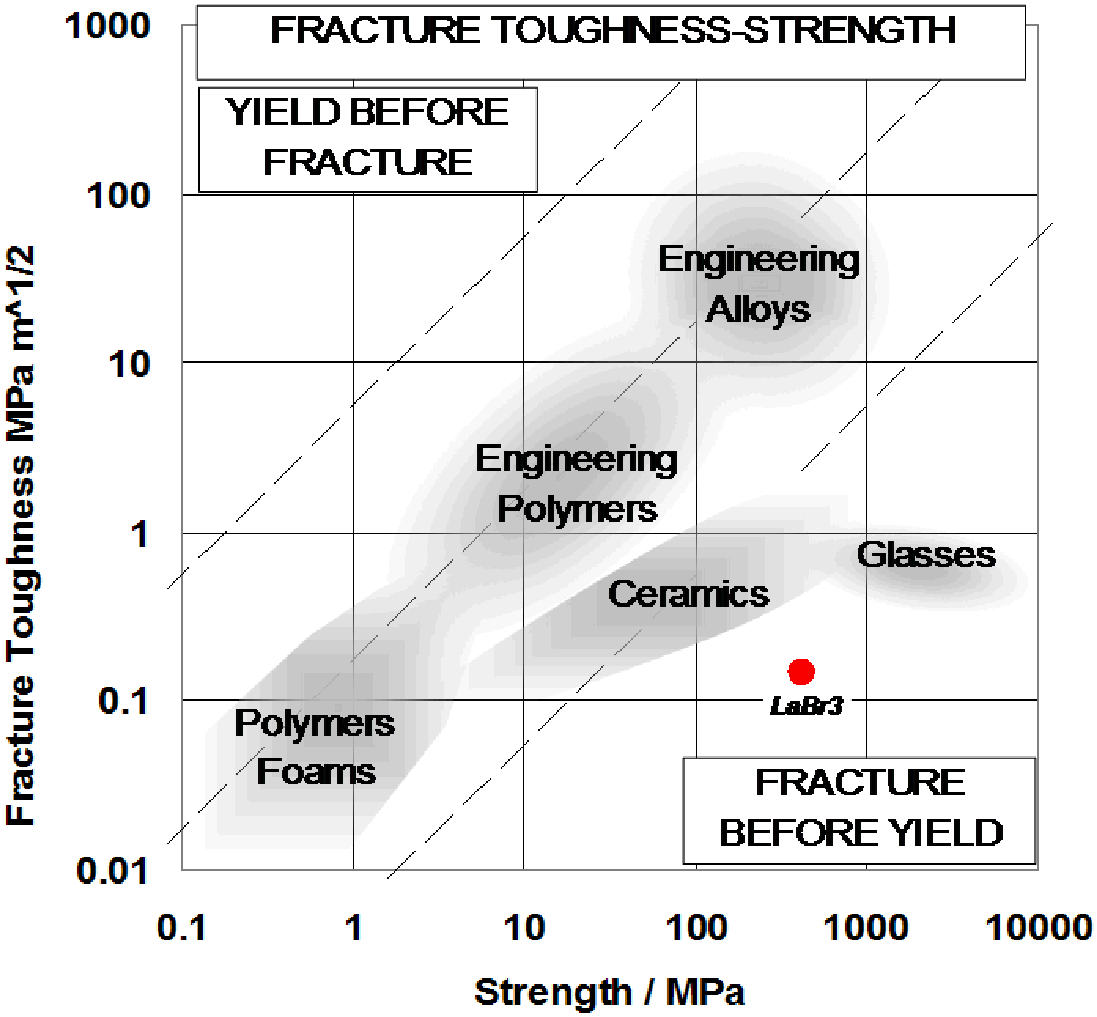

Figure 2. Fracture toughness versus strength for engineering materials and lanthanum bromide. The low toughness of LaBr3 results in cleavage fracture before significant yielding under process stress.

The position of lanthanum bromide on this plot shows that single crystals are extremely fragile, and lie well outside the ranges for useful engineering materials. By contrast, NaI and CsI materials are very ductile and can be extruded or pressed into arbitrary shapes without fracture to form large transparent scintillators. The relative ease of processing these materials is directly related to their cubic crystal structure, giving rise to isotropic thermal expansion and large numbers of independent slip systems.

Strengthening approach

The proposed failure mechanism is initiated by slip on prismatic planes in the LnX3 structure, therefore the fracture toughness in this system is expected to increase in proportion to the yield strength. Methods to strengthen ionic crystals are well known, and their applicability to this system was recently reviewed[6]. Constraints in this application must include minimal alteration of the scintillation process and transparency. This implies that strengthening agents should be incorporated as solid solutions in minimal concentrations. Additives which precipitate or form phases with less than 9-fold coordination of the lanthanide ion will form particles which scatter light, making the crystal cloudy. Therefore the coordination chemistry of potential strengthening agents was considered.

Figure 3 is a plot of coordination number (C.N.) versus anion/cation radius ratio for known AX_3 compounds (X = halogen). A variety of crystal structures are observed in these compounds, with C.N. ranging from 3 to at least 11. The plot indicates potential strengthening agents should have a radius ratio below 2 to maintain the 9-fold coordination of the lanthanide. This constraint actually limits the magnitude of the strengthening, since one effect is purely due to elastic distortions produced by the substituents.

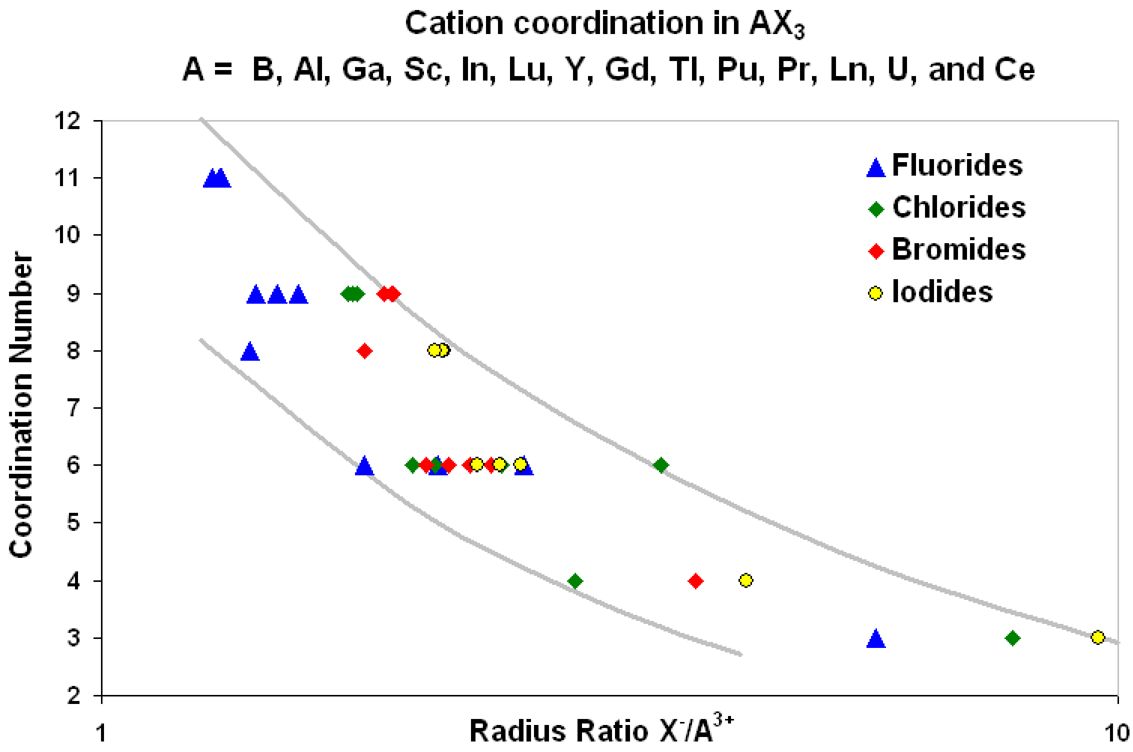

Figure 3. Observed coordination of AX_3 halides showing the trend of decreasing C.N. with increasing anion/cation radius ratio. Cations are listed in order of increasing radius.

The magnitude of the strengthening effects for three known approaches is documented in the literature for a number of ionic crystals. The simplest approach is substitution of one of the matrix ions with a different ion of identical charge; Isovalent substitution.

Isovalent alloying introduces elastic distortions in the lattice due to differences in radii, causing drag forces on dislocation. As noted above, this effect also has the potential to cause phase changes resulting in precipitation. Systems which avoid this problem will require larger concentrations of the strengthening agent, since isovalent substitution relies principally on elastic distortions. The concentration dependence of the yield strength in such systems is typically parabolic, with the maximum strength near 50% by mole.

However, a much more powerful strengthening effect is known for substituent ions of a different charge; Aliovalent substitution. Effects caused by aliovalent substitution include introduction of vacancy concentrations far in excess of equilibrium (due to the requirement of charge neutrality), formation of point defects complexes, tetragonal lattice distortion, and coulombic interaction with charged dislocation cores, in addition to elastic distortions. As should be expected, the energetic price of such substituents results in low solubility limits, which often prevents incorporating large concentrations. However, the magnitude of the strengthening effect is quite large, even for small concentrations; typical aliovalent systems exhibit a square root dependence of yield strength on solute concentration, and order of magnitude increase with parts-per-thousand concentrations are common.

Literature results for the above effects in ionic crystals are shown in Table I. The systems employing isovalent substitution show parabolic strengthening, with critical resolved shear stress τ peaking at over 10 near the 50% alloy composition. Systems having miscibility gaps were also investigated, and the maximum increase in yield strength is due to particle-dislocation interactions in this case. These authors reported cloudy crystals for compositions in the gap. By contrast, the aliovalent systems show factors of 6 to 18 increases in room-temperature strength for concentrations as low as 100 ppm. An interesting case is the Al_2O_3-Ti system, in which Pletka studied both Ti(III) and Ti(IV) additions of equal mole %. The isovalent Ti(III) ion resulted in no significant increase in the yield point, whereas the aliovalent Ti(IV) increased the strength greater than a factor of 2. Isovalent Cr(III) ion produced only a modest increase in strength with 4 times higher concentration.

Table I. Strengthening methods in ionic crystals

System	**Mechanism**	τ/τ_o	**Conc.**	**Dependence**	**Ref**
KCl-KBr	Isovalent substitution	> 10	0-100%	C(1-C)	Katoaka
NaBr-KBr	Isovalent substitution	> 10	0-100%	C(1-C)	Katoaka
NaCl-AgCl	Precipitation	> 10	15-75 %	Misc. gap	Stokes
NaCl-KCl	Precipitation	~ 2	0.5 – 12 %	Misc. gap	Wolfson
NaC1- Ca(II)	Aliovalent subst.	12 - 18	500-900 ppm	$C^{1/2}$	Chin
KC1- Ba(II)	Aliovalent subst.	6 - 15	100-1000 ppm	$C^{1/2}$	Chin
NaBr- Sr(II)	Aliovalent subst.	9 - 18	900-1600 ppm	$C^{1/2}$	Chin
Al2O3-Ti(IV)	Aliovalent subst.	2 (1520 °C)	470 ppm	$C^{1/2}$	Pletka

T. Katoaka and T. Yamada, Japn. J.A.P. 16, 1119 (1977)

R. J. Stokes and C. H. Li, Acta Met., 10, 535 (1962)
G. Y. Chin, et al., J. Am. Ceram. Soc., 56 (1973)
J. B. Pletka, et al., Acta Met., 30,147 IO (1982)
R. G. Wolfson, et al., J. Appl. Phys. 37,704 (1966)
A. Dominguez-Rodriguez et al., J. Am Ceram Soc, 69,281 (1986)

CONCLUSIONS

Cerium and Lanthanum halides form isomorphous alloys with the UCl3 prototype structure. Crystals are highly anisotropic with respect to thermal expansion, plasticity and optical properties, and show perfect cleavage on prismatic planes. Mechanical measurements indicate low fracture toughness, modulus, and yield strength of LaBr3 single crystals, and our analysis of the failure mechanics indicates easy slip in the c direction redistributes residual process stress on prismatic planes, causing cleavage. Cleavage planes are densely packed, and contain the energetically favored Berger's vector, indicating slip and cleavage planes are identical. The limited ductility and profusion of cracking in this system can therefore be attributed to peculiarities of the crystal structure. Work to apply solid solution strengthening methods in collaboration with Kansas State University is in progress, and further work on mechanical properties to determine elasticity constants, slip systems and high temperature deformation mechanisms to enable predictive modeling of stress and fracture during processing is in progress, in collaboration with Washington State University. Sandia will also continue to research thermodynamic and thermophysical properties, determine phase diagrams, solubility limits, and segregation of strengthening agents.

ACKNOWLEDGEMENT

Project funded by the U.S. Department of Energy NA22, National Nuclear Security Administration. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

---

[1] O. Guillot-Noel et al. / Journal of Luminescence 85 (1999) 21,35

[2] C.W.E. van Eijk / Nuclear Instruments and Methods in Physics Research A 471 (2001) 244–248

[3] BrilLanCe380® from Saint-Gobain Crystals and Detectors, http://www.detectors.saint-gobain.com

[4] Structure and properties of lanthanide halides, F. P. Doty, Douglas McGregor, Mark Harrison, Kip Findley, Raulf Polichar, Proc. SPIE 670705 (2007)

[5] Fracture and deformation behavior of common and novel scintillating single crystals
K. O. Findley, J. Johnson, D. F. Bahr, F. P. Doty, and J. Frey, Proc. SPIE 6707, 670706 (2007)

[6] Initial investigation of strengthening agents for lanthanide halide scintillators
M. J. Harrison and F. P. Doty, Proc. SPIE 6707, 67070B (2007)